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(54) Title: POLYSTYRENE-POLYISOPRENE-POLYSTYRENE BLOCK COPOLYMERS, HOT-MELT ADHESIVE COMPOSITIONS, AND ARTICLES PRODUCED THEREFROM (57) Abstract Polystyrene-polyisoprene-polystyrene block copolymers, hot-melt adhesive compositions constituted of polystyrene-polyisoprene-polystyrene block copolymers, and articles of manufacture produced therefrom. These copolymers possess blocks of high average molecular weight polystyrene (12,000 to 20,000) and low overall average molecular weight (60,000 to 110,000) such that when blended in requisite proportions with a compatible tackifier resin, preferably also a secondary tackifying resin or plasticizing oil, and stabilizer, superior hot-melt adhesive compositions can be formed. The hot-melt adhesive compositions possess, inter alia, superior heat resistance, superior static time to failure with low viscosity, good peel adhesion, good tack, and high ability to bond to a polyethylene or polypropylene substrate at temperatures below that which may damage the substrate.		

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POLYSTYRENE-POLYISOPRENE-POLYSTYRENE BLOCK
COPOLYMERS, HOT-MELT ADHESIVE COMPOSITIONS,
AND ARTICLES PRODUCED THEREFROM

This invention relates to polystyrene-
polyisoprene-polystyrene block copolymers, hot-melt
adhesive compositions, and articles formed or
5 constructed therefrom. In particular, it relates to
polystyrene-polyisoprene-polystyrene block copolymers,
and to improved hot-melt adhesive compositions formed
from polystyrene-polyisoprene-polystyrene block
10 copolymers, especially of a type useful in the assembly
of disposable articles, particularly disposable articles
wherein the hot-melt adhesive composition is employed in
the construction to bond a polyethylene or polypropylene
substrate to a tissue, non-woven fabric or absorbent
15 fluff.

It is known to prepare hot-melt adhesive
compositions from polystyrene polyisoprene-polystyrene
and polystyrene-polybutadiene-polystyrene block
20 copolymers. There are numerous uses for hot-melt
adhesives, but whereas one hot-melt adhesive may be
useful in a given application, it may be unsuitable in
another. For example, one particular hot-melt adhesive
might be excellent for bonding together paper, or
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cardboard, but will not form acceptable bonds between certain rubbers, or metals. Moreover, some uses require bonding between substrates formed of different materials, and a given hot-melt adhesive may bond one type of substrate but not the other. Furthermore, it
5 may be necessary that the hot-melt adhesive be applied at relatively low temperature to avoid damage to one or the other of the substrates, or the bond must be flexible and provide adhesive elongation. Certain
10 products, notably disposable articles, for example multi-line products, e.g., disposable diapers, sanitary napkins and bed pads, are exemplary of articles of manufacture which require the use of hot-melt adhesive having such characteristics. Other articles of
15 manufacture requiring the use of hot-melt adhesives include such operations as magazine and book binding, and elastic gluing operations generally.

In the construction of disposable diapers,
20 sanitary napkins, and bed pads, e.g., hot-melt adhesives capable of bonding a non-woven moisture absorbent fabric, or moisture absorbent fluffy material, usually in layers, is applied as a continuous or discontinuous film to a substrate to bond said non-woven fabric or
25 fluffy material thereto. In the construction of multi-line products via present techniques, e.g., in the construction of disposable diapers, a non-woven fabric, or absorbent fluffy material is generally bonded to an inner ply of a soft surfaced material, or tissue, which
30 contacts the wearer's skin. An outer ply of moisture impervious material is adhered thereto via the use of a hot-melt adhesive to minimize moisture, or liquid strike-through. Whereas the adhesive can be sprayed, brushed or otherwise applied upon the surface of a

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substrate as a continuous or discontinuous film, it has become the practice to apply the adhesives as fine lines across the face of a substrate, or as a multi-dot pattern having a large number of adhesive droplets. As a result, these types of construction are generally
5 termed "multi-line" constructions, and the products as "multi-line" products. The hot-melt adhesives used in the production of multi-line products must possess certain adhesive qualities not commonly shared by all
10 adhesives.

In general, e.g., disposable diapers are constituted of a fluid impervious polyethylene, or polypropylene outer sheet and an inner moisture
15 absorbent sheet covered by an inner lining of non-woven tissue. Hot-melt adhesives are applied in the form of fine parallel longitudinal strips to bond the layers together, and hence must possess sufficient adhesive and cohesive strength to provide high bond strength values
20 so that when subjected to stress the constructions cannot be easily separated. It is also necessary that the adhesives withstand high mixing and application temperatures without thermal degradation and loss of adhesive properties, as well as good heat and oxidation
25 resistance on aging. Good adhesive performance is required at elevated temperatures since the disposable articles are worn at body temperature, and also exposed to elevated temperatures during warehousing and
30 shipping. The hot-melt adhesive must have low adhesive viscosity so that it can be applied at low temperature in order to avoid distortion of the polyethylene or polypropylene substrates to which it is applied. Quite obviously, all hot-melt adhesives do not possess these, and other useful properties to the same degree, or even

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to as high degree as would be desired; even those presently commercially used for multi-line constructions. There thus remains a need for improved hot-melt adhesive compositions useful in the assembly of multi-line constructions, and disposable articles of multi-line construction formed from improved hot-melt adhesive compositions. There likewise exists a need for hot-melt adhesives useful in magazine and book binding, and elastic gluing operations generally.

One aspect of this invention is a novel polystyrene-polyisoprene-polystyrene block copolymers, and an improved hot-melt adhesive composition particularly useful in the assembly of disposable articles of manufacture, particularly disposable articles of multi-line construction.

A further aspect of this invention is a hot-melt adhesive composition which has superior heat resistance, superior static time to failure with low viscosity, good peel adhesion, and good tack and high ability to bond to a polyethylene or polypropylene substrate at temperature below that which would be injurious to the substrate.

Another aspect is a disposable article, particularly disposable article of multi-line construction, wherein a polyethylene or polypropylene substrate is bonded to a tissue, or non-woven polyethylene or polypropylene substrate, or both, via the use of said improved hot-melt adhesive composition.

The hot-melt adhesive composition is, in particular, comprised of said polystyrene-polyisoprene-polystyrene block copolymers, the polystyrene blocks of

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which have sufficiently high average molecular weight to provide high shear holding power and shear adhesion failure temperature, and a low overall molecular weight sufficient to provide low viscosity when blended in the requisite proportions with a compatible tackifier resin, preferably also a secondary tackifier resin or plasticizing oil, and stabilizer.

The novel polystyrene-polyisoprene-polystyrene block copolymer is characterized by any of the formulas:

- (1) $B-(AB)_n$ - where n is 2, or greater than 2;
- (2) $A-(BA)_n$ - where n is 1, or greater than 1;
- or (3) $(AB)_n$ - where n is 2, or greater than 2;

wherein, in any of formulas (1), (2), or (3), A is a polystyrene block having an average molecular weight ranging from 12,000 to 20,000, preferably from 14,000 to 19,000. B is a polyisoprene block having an average molecular weight ranging from 30,000 to 70,000, preferably from 35,000 to 60,000, the overall molecular weight of the block copolymer ranges from 60,000 to 110,000, preferably from 70,000 to 95,000, and the polystyrene block A components are present in an amount of at least 27 parts to 50 parts, preferably from 35 parts to 45 parts, per 100 parts by weight of the block copolymer. The A-B-A block copolymer of this invention can thus be a tri-block or multi-block copolymer, and it is characterized by the presence of a B block, or polyisoprene block, located between two polystyrene blocks, or A blocks, which may or may not be terminal end blocks. The A-B-A tri-block copolymer is preferred.

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The hot-melt adhesive composition is, in particular, comprised of from 15 percent to 35 percent, preferably from 20 percent to 30 percent, based on the weight of the hot-melt adhesive composition, of said A-B-A block copolymer; from 45 percent to 70 percent, preferably from 50 percent to 60 percent, based on the weight of the hot-melt adhesive composition, of a compatible primary tackifying resin; from 0 percent to 30 percent, preferably from 5 percent to 20 percent, of a plasticizing oil, or secondary tackifying resin, or both, based on the weight of the hot-melt adhesive composition; and from 0.1 percent to 2 percent, preferably from 0.5 percent to 1.5 percent of a stabilizer, based on the weight of the hot-melt adhesive composition.

These hot-melt adhesive compositions, constituted of an A-B-A block copolymer of intermediate to relatively high styrene content and overall low molecular weight to which the primary tackifying resin, the secondary tackifying resin or plasticizing oil, and stabilizer have been added, have been found to possess properties which are admirably suitable for the construction of disposable articles, particularly disposable articles of multi-line construction wherein the adhesive is applied as fine parallel longitudinal strips, or as a multi-dot pattern of adhesive droplets, to bond together a moisture impervious outer polyethylene or polypropylene sheet and an inner moisture absorbent sheet, or tissue, as used in diaper constructions. These adhesive compositions, with the addition of other materials, such as hydrocarbon waxes, are also useful for magazine and book lining, or book binding, or as elastic glues generally. These hot-melt

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adhesive compositions can be melted, and maintained under a blanketing nitrogen atmosphere, at relatively low to high temperatures without thermal degradation. The compositions can be applied in fluid form to polyethylene and polypropylene substrates as continuous or discontinuous films, suitably as fine lines or as patterns of multi-dots, without any risk of damage to the polyethylene or polypropylene substrate. These hot-melt adhesive compositions have also been found to serve a construction function in binding together an outer sheet, or wrapper overlapped with an absorbent pad as required in the construction of sanitary napkins. The hot-melt adhesive composition applied as a fluid permeates the overlapped area to bind and seal the absorbent pad inside the outer sheet which serves as a wrapper.

The primary tackifying resins useful in the practice of this invention include hydrocarbon resins, synthetic polyterpenes, rosin esters and natural terpenes which are semi-solid or solid at ambient temperatures, and soften or become liquid at temperatures ranging generally from 70°C to 135°C, preferably from 85°C to 120°C. Exemplary of the primary tackifying resins are compatible resins such as (1) natural and modified rosins such as, for example, gum rosin, wood rosin, tall oil rosin, distilled rosin, hydrogenated rosin, dimerized rosin, and polymerized rosin; (2) glycerol and pentaerythritol esters of natural and modified rosins, such as, for example, the glycerol ester of pale, wood rosin, the glycerol ester of hydrogenated rosin, the glycerol ester of polymerized rosin, the pentaerythritol ester of hydrogenated rosin, and the phenolic-modified pentaerythritol ester of

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rosin; (3) copolymers and terpolymers of natured terpenes, e.g., styrene/terpene and alpha methyl styrene/terpene; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from 80°C to 150°C; the latter polyterpene resins generally resulting from the polymerization of terpene hydrocarbons, such as the bicyclic monoterpene known as pinene, in the presence of Friedel-Crafts catalysts at moderately low temperatures; also included are the hydrogenated polyterpene resins; (5) phenolic modified terpene resins and hydrogenated derivatives thereof such as, for example, the resin product resulting from the condensation, in an acidic medium, of a bicyclic terpene and a phenol; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from 70° to 135°C; the latter resins resulting from the polymerization of monomers consisting primarily of olefins and diolefins; also included are the hydrogenated aliphatic petroleum hydrocarbon resins; (7) aromatic petroleum hydrocarbon resins, and mixed aromatic and aliphatic paraffin hydrocarbon resins, and the hydrogenated derivatives thereof; (8) aromatic modified alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof; and (9) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof. The preferred primary tackifying resins for use in the practice of this invention are represented by sub-paragraphs (1), (3) and (7), supra. Suitable secondary tackifying resins are those named species wherein the resin is a liquid at ambient temperature.

Various plasticizing oils are useful in the practice of this invention. The plasticizing oil can be

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used in place of or in combination with the secondary tackifier to reduce viscosity and improve tack properties. Plasticizing oils which have been found useful include olefin oligomers and low molecular weight polymers as well as vegetable and animal oil and their derivatives. The petroleum derived oils which may be employed are relatively high boiling materials containing only a minor proportion of aromatic hydrocarbons (preferably less than 30 percent and, more particularly, less than 15 percent by weight of the oil). Alternately, the oil may be totally non-aromatic. The oligomers may be polypropylenes, polybutenes, hydrogenated polyisoprene, hydrogenated polybutadiene, polypiperylene and copolymers of piperylene and isoprene having average molecular weights between 350 and 10,000. Vegetable and animal oils include glyceryl esters of the usual fatty acids and polymerization products thereof.

The stabilizer, or antioxidant, used in accordance with the practice of this invention includes high molecular weight hindered phenols and multifunctional phenols such as sulfur and phosphorus-containing phenols. Hindered phenols are well known to those skilled in the art and may be characterized as phenolic compounds which also contain sterically bulky radicals in close proximity to the phenolic hydroxyl group thereof. In particular, tertiary butyl groups generally are substituted onto the benzene ring in at least one of the ortho positions relative to the phenolic hydroxy group. The presence of these sterically bulky substituted radicals in the vicinity of the hydroxyl group serves to retard its stretching frequency and, correspondingly, its reactivity; this steric hindrance thus providing the phenolic compound

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with its stabilizing properties. Representative hindered phenols include: 1,3,5-trimethyl 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl) benzene; pentaerythrityl tetrakis-3 (3,5-di-tert-butyl-4-hydroxyphenyl) propionate; n-octadecyl-3 3,5-di-tert-butyl-4-hydroxyphenyl)-propionate; 4,4'-methylenebis (2,6-tert-butylphenol); 4,4'-thiobis (6-tert-butyl-o-cresol); 2,6-di-tertbutylphenol; 6-(4-hydroxyphenoxy)-2,4-bis(n-octyl-thio)1,3,5 triazine; di-n-octadecyl 3,5-di-tert-butyl-4-hydroxy-benzylphosphonate; 2-(n-octylthio) ethyl 3,5-di-tert-butyl-4-hydroxy-benzoate; and sorbitol [hex 3-(3,5-di-tert-butyl-4-hydroxyphenyl)-propionate.]

The hot-melt adhesive composition is prepared for use by blending the A-B-A block copolymer with the primary tackifying resin, the secondary tackifying resin or plasticizing oil, and stabilizer, in any order or sequence, or these materials can be added together simultaneously to form the adhesive composition. In commercial practice it would be expected that the primary tackifying resin and copolymer, with or without the simultaneous addition of the secondary tackifying resin or plasticizing oil, and stabilizer, would be blended together at sufficiently elevated temperature to form a fluid melt. For example, the copolymer can be blended with the solid compatible primary tackifying resin at temperatures ranging from 130°C to 200°C, preferably from 150°C to 180°C, to form a fluid melt. The secondary liquid tackifying resin, or plasticizing oil, and stabilizer, can then be added to the melt. Alternatively, the fluid melt can be prepared with all components of the adhesive composition initially present.

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The following non-limiting examples, and comparative data, bring out the more salient features of the invention. All parts are given in terms of weight units except as may otherwise be indicated.

5 In conducting the following tests the composition and properties of the neat A-B-A block copolymers which were prepared for making the adhesive compositions were determined by techniques "a", "b" and "c". In evaluating the performance characteristics of
10 the adhesive compositions produced from the A-B-A block copolymers test procedures "d" through "h" were employed, to wit:

15 a. Styrene content - of the experimental A-B-A block copolymers was determined from the proton nmr spectra. Samples were dissolved in a mixture of deuterated tetrachloroethane/tetrachloroethylene, and analyzed on a Bruker 90 MHz spectrometer. Styrene
20 content was calculated from the spectra by the method of V.D. Mochel, Rubber Chem. and Tech., 40, 1200 (1967).

 b. Molecular Weight - of the experimental A-B-A block copolymers was determined by GPC, using the
25 method described by J. R. Runyon, et al, J. Polym. Sci. 13, 2359 (1969).

 c. Melt Flow Rate (MFR) - of the experimental A-B-A copolymers was determined according to ASTM method
30 D-1238-82, using condition "G" (200°C, 5 Kg weight).

 d. Adhesive Melt Viscosity (ASTM D-3236) - Melt viscosities were measured at a temperature of 130°C, using a Brookfield Thermosel viscometer. Low adhesive viscosities are a necessity for processing in multi-line, spray, and fiberization equipment. In

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addition, the viscosity must be low at relatively low processing temperatures in order to avoid distortion of the polyolefin backing when hot adhesive is applied.

5 e. Shear Adhesion Failure Temperature (SAFT) -
is a measure of the ability of the bond to withstand an
elevated temperature rising at 10°F/15 min. (5.5°C/min)
under a constant force which pulls the bond in the shear
mode. Bonds 1 inch by 1 inch (25 mm by 25 mm) were
10 formed of adhesive, on a Mylar (polyester) backing, to a
stainless steel panel, using a 4.5 lb. (2 kg) rubber
roller. The panel was suspended vertically in an oven
at 32°C, and allowed to come to equilibrium. A 1 kg
weight was suspended from the free end of the adhesive
15 tape, and the temperature was raised at 10°F/15 min
(5.5°C/15 min). The temperature at which the tape and
weight fell from the panel was recorded. SAFT was
reported as the average of three such determinations.
Adhesives possessing high failure temperatures are
20 essential for the assembly of disposable articles, which
are often subjected to very high temperatures during
storage and shipping. In addition, these articles are
used (worn) at body temperature.

25 f. Shear Holding Power (Static Time to Failure
Bond Test) - The cohesive strength of the adhesives was
determined according to the general procedures outlined
in PSTC-7 and ASTM D-3654. A 1 inch by 0.5 inch (25 mm
by 13 mm) bond was applied to a stainless steel panel
30 with a 4.5 lb (2 kg) rubber roller. The plate was
suspended vertically and allowed to equilibrate at 35°C.
A 1 kg weight was suspended from the free end of the
tape. The time at which the tape and weight fell from
the panel was recorded. The shear hold (in min) was
reported as the average of four such determinations.

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Long failure times are desirable, since they indicate strong bonds, which are essential in certain areas of the disposable constructions, which are subjected to considerable stress during use.

5 g. 180 Degree Peel Adhesion - of the adhesives
was determined according to the procedures outlined in
PSTC-1 of the Pressure Sensitive Tape Council. A 1 inch
by 6 inch (25 mm by 152 mm) strip of the adhesive tape
10 (2 mil (0.05 mm) Mylar backing) was applied to a
stainless steel panel with a 4.5 lb. (2 kg) rubber
roller. The tape and panel were conditioned 24 hrs.
under ASTM conditions of temperature and humidity prior
to testing. The tape was then peeled back over itself
15 at 180° in a tensile tester at a constant crosshead
speed of 12 in/min. (305 mm/min). The average force
required to peel the tape from the panel was recorded.
The 180 peel (lb/in (N/m)) was reported as the average
of three such determinations.

20 h. Loop Tack - is that property of a pressure
sensitive adhesive, which causes it to adhere to a
surface instantly using no external pressure to secure a
thorough bond. Loop tack is measured as the force
25 resisting peeling of a tape at 90° from a standard
surface upon which it has been applied under no other
pressure than the weight of the tape itself. Loop tack
was measured using a tensometer with a crosshead speed
of 20 in/min (508 mm/min). The tape contact area was 1
30 inch by 1 inch (25 mm by 25 mm). The loop tack (lb/in
(N/m)) was reported as the average of three
determinations. (Modified version of PSTC-5)

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Example 1

To a 2.6 liter autoclave were charged 1900 ml of cyclohexane and 88.1 gm of styrene monomer. The mixture was heated to 60°C and 3.7 ml of a 1.4 molar solution of sec-butyllithium initiator in cyclohexane was added. After 40 minutes, when analysis of the reaction mixture indicated that polymerization of the styrene monomer was complete, the reaction temperature was reduced to 50°C, and 116.7 gm of isoprene was added. After 45 minutes, no unreacted isoprene was detected. The living styrene-isoprene diblock polymer was then coupled to form a styrene-isoprene-styrene tri-block polymer by adding 32.0 ml of 0.12 M 1,2-dibromoethane in cyclohexane over a period of 11 minutes. Analysis of the product by gel-permeation chromatography (GPC) indicated that the tri-block polymer had a peak molecular weight of 76,800, and contained approximately 12 percent residual diblock. From the proton NMR spectrum of the product, it was determined that it contained 41.7 weight percent styrene. The solvent was removed from the polymer solution under vacuum at 90°C.

Example 2

Using a procedure essentially identical to that of Example 1, 94.3 gm of styrene monomer was polymerized using 4.2 ml of 1.4 molar sec-butyllithium solution, followed by addition of 110.7 gm of isoprene. The resulting living polymer was then coupled by addition of 36.6 ml of 0.12 molar 1,2-dibromoethane. Analysis of the product, via the means described by reference to Example 1, shows that the triblock polymer had a peak

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molecular weight of 76,500, and that it was constituted of 44.8 weight percent styrene.

Example 3

5 Using a procedure essentially identical to that of Example 1, 81.8 gm of styrene monomer was polymerized using 4.2 ml of 1.4 molar sec-butyllithium solution, followed by addition of 122.7 gm of isoprene. The resulting living polymer was then coupled by addition of
10 36.5 ml of 0.12 molar 1,2-dibromoethane. This product triblock polymer was found to have a peak molecular weight of 76,500, and was constituted of 38.6 weight percent styrene.

15 The pertinent properties of the block copolymers produced as described by Examples 1 through 3 are given in the Table below, particular reference being made to Columns 1 through 6 of the Table.

20 The following tabulates the amounts of the cyclohexane solvent, the initiator, the styrene monomer, the isoprene monomer, and dibromoethane employed in the preparation of additional polystyrene-polyisoprene-
25 polystyrene (S-I-S) block copolymers, for comparative purposes, wherein one or more of the properties fall outside that required to produce a satisfactory adhesive, i.e., the average molecular weight required for the polystyrene end blocks, the polyisoprene mid
30 block, overall molecular weight, or the weight percent styrene.

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<u>Comparative Examples</u>		<u>4</u>	<u>5</u>	<u>6</u>	<u>7</u>
5	Milliliters 1.4 M/L sec-butyllithium	2.6	3.6	4.9	2.9
	Grams of Styrene Monomer	44.8	55.0	65.3	55.0
	Grams of Isoprene Monomer	158.7	148.7	138.7	148.7
	Milliliters 0.12 M/L dibromoethane	23.1	32.9	44.0	25.5

10

The pertinent properties of SIS block copolymers produced in Comparative Examples 4 through 7 are given in the Table below, particular reference being made to Columns 1 through 6 of the Table.

15

For comparative purposes also, two additional block copolymers of the polystyrene-polybutadiene-polystyrene (S-B-S) type were prepared in generally similar manner except that in these instances

20

(Comparative Examples 8 and 9, respectively) accurately measured amounts of 1,3-butadiene was used in place of the isoprene in the preparation procedure.

25

The following tabulates the amounts of cyclohexane solvent, the initiator, the styrene and butadiene monomers, respectively, and dibromoethane employed in the preparation of the rubbers used in Comparative Examples 8 and 9, respectively.

30

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	<u>Comparative Examples</u>	<u>8</u>	<u>9</u>
	Kg Cyclohexane Solvent	12.6	11.8
5	Milliliters 0.295 M/L sec-butyllithium	228.2	314.2
	Grams of Styrene Monomer	791.8	1090.0
	Grams of Butadiene Monomer	1093.4	1505.2
10	Milliliters 1.16 M/L dibromoethane	43.5	59.9

15 The pertinent properties of the SBS block copolymers produced by Comparative Examples 8 and 9 are given in the Table below, specific reference being made to Columns 1 through 6 of the Table.

20 Additionally, for comparative purposes, several S-I-S block copolymers and an S-B-S block copolymer were obtained from commercial sources. Comparative Examples 10-12 thus describe adhesive compositions formed from S-I-S block copolymer produced by Shell Chemical Company (Comparative Examples 10 and 11) and Enichem Americas, Inc. (Comparative Example 12), respectively.

25 Comparative Example 13 describes an adhesive composition formed from S-B-S block copolymer produced by Firestone Tire and Rubber Company.

30 Adhesive compositions were prepared by combining 100 parts of the block copolymer, 220 parts of ECR-149B (an aromatic modified aliphatic hydrocarbon tackifier resin, available from Exxon Chemical), 80 parts of Tufflo 6056 (a plasticizer oil available from Lyondell Petroleum Company), and 3 parts of Irganox 1010 (a stabilizer available from Ciba-Geigy), to produce a homogeneous adhesive blend. The adhesive was coated on

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2 mil thick Mylar (polyester) backing, to produce a
1.5 mil thick film, of adhesive.

The performance characteristics of the block
copolymers are given in the Table, the adhesive
5 formulations for the S-I-S "rubbers" of this invention,
designated as Examples 1, 2 and 3, being set out for
comparison with adhesive formulations prepared from
S-I-S rubbers not of this invention (Comparative
10 Examples 4-7 and 10-12) and S-B-S rubbers (Comparative
Examples 8-9 and 13). Columns 1 and 2 of the Table
identifies the specific test run and type of rubber
tested. Columns 3-6 identifies the total weight percent
15 styrene content of the rubber, the overall molecular
weight (X1000) of a rubber, the molecular weight of the
polyisoprene (X1000), and the molecular weight of the
polystyrene (X1000), respectively. Columns 7-12
describe the results of the tests conducted on each of
the adhesive formulations, viz the adhesive viscosity,
20 SAFT, holding power, peel and tack. It is clear that
the adhesive compositions of this invention, i.e.,
Examples 1-3, exhibit superior SAFT (high temperature
resistance), superior holding power (static time to
failure), equivalent or lower viscosity, and equivalent
25 peel and tack.

30

Table (continued)

Rubber	Type	Wt % Styrene	Overall MW/1000	Poly-isoprene MW/1000	Poly-styrene MW/1000	Adhes. Visc. 130°C Cps (Pa-s)	SAFT (°C)	35°C Hold (min)	180 PEEL SS, Lb/in (N/m)	180 PEEL PE, Lb/in (N/m)	Loop Tack SS, Lb/in (N/m)
Comp. Ex. 7	SIS	28.8	121.9	86.8	17.6	32,500 (32.5)	77.7	>3900	-	-	-
Comp. Ex. 8	SBS	42.0	61.3	-	12.9	10,600 (10.6)	64.0	1711	3.8 (665)	-	6.7 (1173)
Comp. Ex. 9	SBS	42.0	66.0	-	13.9	9,000 (9)	66.0	>3900	4.2 (735)	-	6.7 (1173)
Comp. Ex. 10 (KRATON D1107)	SIS	14.5	150.0	128.3	10.9	26,800 (26.8)	47.0	80	5.3 (928)	2.6 (455)	5.8 (1015)
Comp. Ex. 11 (KRATON D1111)	SIS	22.8	143.0	110.4	16.3	35,500 (35.5)	71.9	2889	6.6 (1155)	2.9 (508)	6.7 (1173)
Comp. Ex. 12 (EUOPRENE SOL T 193 B)	SIS	24.2	109.0	82.6	13.2	12,100 (12.1)	64.1	741	5.5 (963)	2.9 (508)	6.5 (1138)
Comp. Ex. 13 (STEREON 840 A)	SBS	42.3	78.4	-	-	14,700 (14.7)	59.0	556	4.3 (753)	2.7 (473)	6.5 (1138)

Note 1: "KRATON" is a trademark of Shell Chemical Company

Note 2: "EUOPRENE" is a trademark of Enichem Americas, Inc.

Note 3: "STEREON" is a trademark of Firestone Tire and Rubber Company.

Note 4: "Comp. Ex." is Comparative Example.

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Continuing reference to the Table, Examples 1, 2 and 3 show the performance of adhesive compositions prepared from S-I-S block polymers whose percent styrene, overall molecular weight, polyisoprene molecular weight, and polystyrene molecular weight are all within the preferred ranges of the S-I-S block copolymer required for the practice of this invention. It is required that all four of these parameters fall within the ranges expressed in order to obtain this superior adhesive performance. Comparative Examples 4 through 7 represent adhesive compositions prepared from S-I-S block copolymers wherein one or more of the requisite parameters -- viz. percent styrene, overall molecular weight, polyisoprene molecular weight and polystyrene molecular weight -- fall outside those requirements which are necessary to obtain superior hot-melt adhesives. The same is true of the adhesive compositions prepared from commercially available S-T-S block copolymers as represented by Comparative Examples 10 (Kraton D 1107), 11 (Kraton D 1111), and 12 (Europrene SOL T 193 B), all of which are prepared from S-I-S block copolymers having one or more of the four parameters which fall outside of the requisite ranges. As shown by the Table, the adhesive compositions of Examples 1, 2 and 3 clearly exhibit the best combination of low adhesive viscosity, high SAFT, high 35°C Hold, and good peel and tack to stainless steel and polyethylene.

The performance of the adhesive compositions prepared from S-I-S block copolymers, as illustrated by reference to Examples 1, 2 and 3, are also shown to be superior to those prepared from S-B-S block copolymers (Comparative Examples 8, 9 and 13). This is surprising,

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because Stereon 840 A (Comparative Example 13) has been held out as a S-B-S block copolymer of choice for the production of hot-melt adhesives, and the performance of adhesive compositions prepared from this particular S-B-S block copolymer has been exemplified as superior to
5 adhesive compositions prepared from earlier S-I-S block copolymers, as disclosed in U.S. Patent 4,526,577. The performance of adhesive compositions made from Stereon 840 as contrasted with the adhesive compositions of this invention, as shown by Examples 1, 2 and 3, however, is
10 poor. Relative to an adhesive composition prepared from Stereon 840 A, adhesive compositions made from S-I-S block copolymers pursuant to the practice of this invention have lower viscosity, much higher SAFT, much
15 longer shear holding times at 35°C, and better 180°C Peel to polyethylene. Moreover, the adhesive compositions of this invention, as exemplified by Examples 1, 2 and 3, are also shown to be superior to an adhesive composition prepared from two specially prepared S-B-S block
20 copolymers (Comparative Examples 8 and 9).

An adhesive composition useful for magazine or book binding can also be formed from the hot-melt adhesive composition of this invention by the further
25 addition to the hot-melt adhesive composition of up to about 5 percent, preferably from 0.5 to 5 percent, based on the weight of the hot-melt adhesive composition, of a hydrocarbon or petroleum derived wax. Exemplary petroleum derived waxes are, e.g., paraffin and
30 microcrystalline waxes having melting points within a range of from 55°C to 110°C, as well as low molecular weight polyethylene and Fischer-Tropsch waxes.

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It is apparent that various modifications and changes can be made without departing the spirit and scope of the invention.

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Claims

1. A composition of matter useful in forming hot-melt adhesives which comprises an A-B-A block copolymer wherein the B component is polyisoprene having an average molecular weight ranging from 30,000 to 70,000, the A component is polystyrene having an average molecular weight ranging from 12,000 to 20,000, the overall molecular weight of the block copolymer ranges
5 from 60,000 to 110,000 and wherein the A component is present in an amount of at least 27 parts to 50 parts per 100 parts by weight of the block copolymer.
2. A composition as claimed in Claim 1
10 wherein the average molecular weight of the B component of the A-B-A block copolymer ranges from 35,000 to 60,000, the average molecular weight of the A component ranges from 14,000 to 19,000, the overall molecular
15 weight of the copolymer ranges from 70,000 to 95,000 and wherein the A component is present in an amount ranging from 35 parts to 45 parts per 100 parts by weight of the copolymer.
- 20 3. A hot melt adhesive composition useful in the assembly of disposable articles which comprises
from 15 percent to 35 percent based on the weight of the hot-melt adhesive composition, of an A-B-A block copolymer as claimed in Claim 1,
25 from 45 percent to 70 percent of a compatible

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primary tackifying resin, based on the weight of the hot-melt adhesive composition,

from 0 percent to 30 percent of a plasticizing oil or secondary tackifying resin, based on the weight of the hot melt adhesive composition, and

5 from 0.1 percent to 2 percent of a stabilizer, based on the weight of the hot-melt adhesive composition.

4. A Composition as claimed in Claim 3
10 wherein the hot melt adhesive composition contains from 20 percent to 30 percent of the copolymer.

5. A composition as claimed in Claim 3
15 wherein the hot-melt adhesive composition additionally contains up to about 5 percent, based on the weight of the hot-melt adhesive composition, of a hydrocarbon wax sufficient to form an adhesive composition useful for lining magazines or books.

20 6. A disposable article comprising a polyethylene or polypropylene substrate bonded to a tissue, non-woven, polyethylene or polypropylene, substrate using a hot-melt adhesive composition which comprises
25 from 15 percent to 35 percent, based on the weight of the hot-melt adhesive compositions, of an A-B-A block copolymer as claimed in Claim 1,

30 from 45 percent to 70 percent of a compatible primary tackifying resin, based on the weight of the hot-melt adhesive composition,

from 0 percent to 30 percent of a plasticizing oil or secondary tackifying resin, based on the weight of the hot-melt adhesive composition, and

from 0.1 percent to 2 percent of a stabilizer,

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based on the weight of the hot-melt adhesive composition.

7. A disposable article as claimed in Claim 6, wherein the average molecular weight of the B component of the A-B-A block copolymer ranges from 35,000 to 60,000 the average molecular weight of the A component ranges from 14,000 to 19,000, the overall molecular weight of the copolymer ranges from 70,000 to 95,000, and wherein the A component is present in amount ranging from 35 parts to 45 parts per 100 parts by weight of the copolymer.

8. A disposable article as claimed in Claim 6, wherein the primary tackifying resin is any compatible resin or mixture thereof selected from (1) natural and modified rosins; (2) glycerol and pentaerythritol esters of natural and modified rosins; (3) copolymers and terpolymers of natured terpenes; (4) polyterpene resins having a softening point, as determined by ASTM method E28-58T, of from about 80° to 150°C; (5) phenolic modified terpene resins and hydrogenated derivatives thereof; (6) aliphatic petroleum hydrocarbon resins having a Ball and Ring softening point of from 70° to 135°C; (7) aromatic petroleum hydrocarbon resins, and mixed aromatic and aliphatic paraffin hydrocarbon resins, and the hydrogenated derivatives thereof; (8) aromatic modified alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof; and (9) alicyclic petroleum hydrocarbon resins and the hydrogenated derivatives thereof.

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9. A disposable article as claimed in Claim 6 wherein the disposable article is selected from diapers, sanitary napkins and bed pads.

5 10. A disposable article as claimed in Claim 6 wherein the adhesive component of the disposable article is applied as a discontinuous phase, as a continuous phase, as fine parallel longitudinal strips or as a multi-dot pattern of adhesive droplets.

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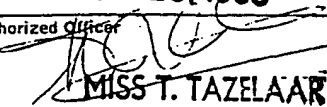
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INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/04408

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ⁶ According to International Patent Classification (IPC) or to both National Classification and IPC IPC5: C 09 J 153/02, C 08 L 53/02, A 16 L 15/24						
II. FIELDS SEARCHED <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Minimum Documentation Searched⁷</div> <table style="width: 100%; border-collapse: collapse;"> <tr> <td style="width: 25%; border-bottom: 1px solid black;">Classification System</td> <td style="border-bottom: 1px solid black;">Classification Symbols</td> </tr> <tr> <td style="height: 40px; vertical-align: bottom;">IPC5</td> <td style="vertical-align: bottom;">C 08 L; C 09 J; A 61 L</td> </tr> </table> <div style="text-align: center; border-top: 1px solid black; border-bottom: 1px solid black;">Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in Fields Searched⁸</div>			Classification System	Classification Symbols	IPC5	C 08 L; C 09 J; A 61 L
Classification System	Classification Symbols					
IPC5	C 08 L; C 09 J; A 61 L					
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹						
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³				
X	DE, A1, 2942128 (BASF AG) 30 April 1981, see page 3, line 4 - line 10; page 5, line 27 - page 6, line 2; page 8, line 15 - line 26; page 11, line 28 - line 30; claim 1	1-5				
A	--	6-8				
X	US, A, 4172860 (FEENEY ET AL) 30 October 1979, see column 1, line 6 - line 10; column 2, line 19 - line 24; column 2, line 29 - line 42	1-2				
X	DE, B2, 1594267 (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 28 August 1969, see column 4, line 28 - line 39; claim 2	1-5				
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁰</p> <p>^{"A"} document defining the general state of the art which is not considered to be of particular relevance</p> <p>^{"E"} earlier document but published on or after the international filing date</p> <p>^{"L"} document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>^{"O"} document referring to an oral disclosure, use, exhibition or other means</p> <p>^{"P"} document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 50%;"> <p>^{"T"} later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>^{"X"} document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>^{"Y"} document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>^{"&"} document member of the same patent family</p> </div> </div>						
IV. CERTIFICATION						
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report					
16th November 1990	<div style="font-size: 1.2em; font-weight: bold;">04 DEC. 1990</div>					
International Searching Authority	Signature of Authorized Officer					
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III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No
A	US, A, 3736281 (THOMAS E RUSSELL) 29 May 1973, see column 3, line 3 - line 12; claim 2 --	1-5
A	US, A, 3784587 (THOMAS G. CHAMBERS) 8 January 1974, see abstract; example 2 --	1-5
A	US, A, 4540415 (RALF KORPMAN) 10 September 1985, see column 4, line 9 - line 32; claims 1,4 -- -----	3

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. PCT/US 90/04408**

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This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 27/09/90. The European Patent office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE-A1- 2942128	30/04/81	NONE	
US-A- 4172860	30/10/79	NONE	
DE-B2- 1594267	28/08/69	BE-A- 695394	13/09/67
		DE-A-C- 1794415	24/02/77
		FR-A- 1513990	00/00/00
		GB-A- 1116426	00/00/00
		NL-A- 6703770	15/09/67
		US-A- 3427269	11/02/69
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		GB-A- 1429376	24/03/76
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		AU-D- 1136683	18/08/83
		GB-A-B- 2114449	24/08/83
		JP-A- 58156002	16/09/83

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